

# Electrochemical and corrosion behaviour of copper shape memory alloy in NaCl solution

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**Vrsalović, Ladislav; Ivanić, Ivana; Gudić, Senka; Gojić, Mirko**

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## Electrochemical and corrosion behaviour of copper shape memory alloy in NaCl solution

Ladislav Vrsalović<sup>1</sup>, I. Ivanić<sup>2</sup>, S. Gudić<sup>1</sup>, M. Gojić<sup>2</sup>

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### Abstract

*This paper presents a review of electrochemical and corrosion investigations on behaviour of CuAlNi and CuAlMn alloys in NaCl solutions, which were carried out within the framework of the project IP-2014-09-3405 “Design of microstructure and functional properties of copper-based shape memory alloys”, supported by the Croatian Science Foundation. The influence of alloys heat treatment on their corrosion behaviour was investigated, as well as the influence of chloride concentration, pH values and electrolyte temperatures. Cu-shape memory alloys were produced by continuous vertical casting and melt spinning method. Investigations were conducted by electrochemical methods such as open circuit current measurement method, electrochemical impedance spectroscopy method, linear and potentiodynamic polarization. Corroded specimens characterization was obtained by optical and scanning electron microscope. Analysis of the corrosion product composition was carried out by EDS method.*

### Introduction

In recent years many researchers have focused their interests in smart materials development and investigation its properties, as this promising materials can meet the technological demands in various industries [1-5]. A smart material is a material which reacts to a stimulus or environmental change [6, 7]. Shape memory alloys (SMAs) are regarded as smart materials, as they exhibit physical recovery to their original shapes after being deformed upon heating to critical temperatures. This unique effect of returning to an original geometry after a large inelastic deformation is known as the shape memory effect (SME). Shape memory phenomenon results from crystalline phase change known as “thermoelastic martensitic transformation”. At temperatures below transformation temperature, shape memory alloys are martensitic. In this condition, their microstructure is characterized by “self-accommodating twins”. The martensite is soft and can easily be deformed by de-twinning. Heating above the transformation temperature recovers the original shape and converts the material to its high strength, austenitic condition [4,8-10]. NiTi alloys are one of the most common used shape memory alloys in practice due to their outstanding properties such as excellent shape memory effect, unique superelasticity, low elastic modulus, high corrosion resistance and biocompatibility [11-14]. Their disadvantages lies in high production costs and low transformation temperatures (-100 to 100 °C) which is why they are often replaced by cheaper Cu-SMA alloys in in less demanding applications [15,16]. The main advantages of Cu-based alloys are their low price, relatively simple fabrication procedure, and high electrical and thermal conductivity compared to other shape memory alloys. Among Cu-based SMAs, CuAlNi, CuAlZn and CuAlMn alloys are extensively investigated [9,10,16-21]. Shortcomings of these alloys such as brittleness and low mechanical strength are closely related to microstructural characteristics such as coarse and large grain size, high elastic anisotropy and the segregation of secondary phases along the grain boundaries [22-24]. CuAlNi and CuAlZn alloys are brittle and susceptible to intergranular fracture while CuAlMn shape memory alloy shows better ductility and good strain recovery, which is correlated with decreasing the degree of order of the  $\beta$  parent phase. Other advantages of CuAlMn alloys compared to other Cu-based SMAs are higher shape memory strain,

larger recovery power, better ductility, and higher damping capacity [25]. To overcome above mentioned problems, several ways have been identified by the researcher so far such as thermomechanical processing, use of micro-alloy elements for grain refinement and use rapid solidification process in alloys production [15,23,26,27]. One of the possible solution is the addition of grain-refining elements such as Ti and B which leads to the formation of more  $\beta$ -phase nucleation sites [28,29]. Titanium as micro alloying elements tend to form precipitates such as the  $\text{Cu}_2\text{AlTi}$ . The addition of Ti and B can refine the grains by forming particles  $\text{TiB}_2$  which can hinder grain growth during annealing [30]. Generally there are four advantages of rapid solidification over the slow conventional solidification techniques. These are an ability to form metastable phases, increasing the solubility above the equilibrium solubility, decreasing the segregation of additions and refining the microstructure [10,31,32].

Most of the research papers deals with the microstructure, mechanical and shape memory properties and possible practical applications of Cu-SMA neglecting corrosion investigations of these materials which are very important for their practical use [2,3,6,10,17,18,20,22,25]. Corrosion resistance of CuAl alloys has been attributed to formation of protective layer of alumina along with copper chloride and oxide [33-35]. Aluminium has a greater affinity towards oxygen than copper and higher stability of  $\text{Al}_2\text{O}_3$  than  $\text{Cu}_2\text{O}$ . Some researchers attributed the enhancement of corrosion resistance to the formation of surface duplex layer of oxide compounds composed of  $\text{Cu}_2\text{O} \times \text{Al}_2\text{O}_3 \times x\text{H}_2\text{O}$  [36]. The presence of nickel is also important in the passivation of CuNi alloys because of its incorporation in the Cu(I) oxide, which is formed on the corroded surface of the alloy and reduce the number of cation vacancies that normally exist in Cu(I) oxide [34-36]. Saud et al. reported that an increment in Mn content up to 0.7 wt.% improved the corrosion resistance of CuAlNi alloy [37]. Saud and associates have also studied effect of the addition of fourth alloying element (Ti or Mn) and Ag nanoparticles on corrosion characteristics of CuAlNi alloy and they found enhancement of corrosion resistance in both investigations [15,23].

Presented investigations in this paper was focussed on corrosion behaviour of different CuAlNi and CuAlMn alloys produced by vertical casting methods and alloy ribbons produced by rapid solidification using melt spinning method in NaCl solution.

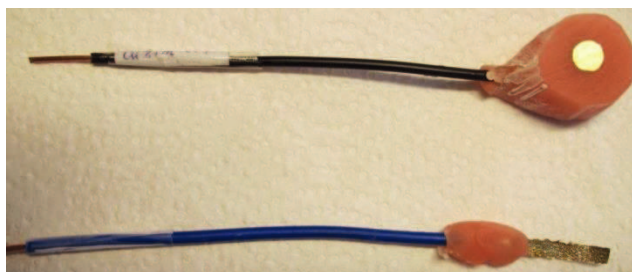
## Experimental procedure

CuAlNi and CuAlMn alloy were manufactured by vertical continuous casting method under protective argon atmosphere, in a form of cylindrical rod with 8 mm in diameter. The chemical composition of the CuAlNi examined by EDS analysis was 84.67 % Cu, 11.29 % Al and 4.05 % Ni (wt%) and composition of the CuAlMn was 82.3 % Cu, 8.3 % Al and 9.4 % Mn (wt.%). After casting, some CuAlNi alloy rod was solution annealed at 850 °C (K1) and 920 °C (K2) for 60 minutes followed by water quenching (WQ) in the room temperature water.

For electrochemical measurements, Cu-SMA alloy rods were cut to obtain small cylinders, 1 cm in height and 8 mm in diameter, from which the electrodes were prepared. Cu-SMA cylinders were soldered to the insulated copper wire to ensure good electrical contact, followed by their insulation with polyacrylate leaving only one non-insulated roller base of 0.502 cm<sup>2</sup> which was used as a working surface in contact with the electrolyte. Before each experiment, the working electrode was ground with a Metkon Forcipol 1 V grinding/polishing machine, using successive grades of emery papers down to 2000 grit, polished with  $\text{Al}_2\text{O}_3$  polishing suspension (particle size of 0.3  $\mu\text{m}$ ) and then ultrasonically washed in ethanol solution.

Cu-SMA rapidly solidified ribbons were produced with the single roll melt spinning apparatus. The cast precursors were inserted into the graphite crucible and inductively melted in Ar atmosphere and sprayed through the nozzle into the cooled rotating copper wheel. The ribbon samples for the electrochemical measurements were prepared by cutting to the appropriate dimensions and then soldered on an insulated copper wire to gain proper electrical contact. Soldered joint spots are

insulated with polyacrylate protective mass to prevent the evaluation of galvanic corrosion in contact with the electrolyte. Due to its small thickness, mechanical treatment of Cu-SMA ribbons by grinding and polishing could not be performed, so the surface of the electrode was processed by ultrasonic degassing in ethanol, washed with deionized water and immersed in the electrolyte. Figure 1 shows Cu-SMA electrodes prepared for electrochemical measurements.



*Figure 1. Cu-SMA electrodes prepared for electrochemical measurements*

Princeton Applied Research PAR M273A potentiostat/galvanostat connected with PC was used to perform electrochemical investigations. All measurements were taken in double wall glass cell which allowed maintenance of desired electrolyte temperature, equipped with saturated calomel electrode as reference electrode, Pt-sheet electrode as counter electrode and prepared working electrode. Investigations were performed in 0.9% NaCl solution pH = 7.4 and  $T = 37\text{ }^{\circ}\text{C}$ . Electrolyte solution was purged with Ar for 20 minutes prior working electrode immersion in electrolyte, and purging were continued during the electrochemical measurement with very weak intensity. The evaluation of corrosion behaviour of investigated alloys was performed by open circuit potential measurements ( $E_{OC}$ ) in 60 minutes time period, linear polarisation method in the potential region of  $\pm 20\text{ mV}$  around corrosion potential, with the scanning rate of  $0.2\text{ mV s}^{-1}$  and potentiodynamic polarisation method in the potential region of  $-0.250\text{ V}$  from  $E_{OC}$  to  $1.2\text{ V}$  for casting alloy samples and to  $0.7\text{ V}$  for ribbon alloy samples, with the scan rate of  $0.5\text{ mV s}^{-1}$ . Impedance spectra were recorded at  $E_{OC}$  in the frequency range from  $50\text{ kHz}$  to  $30\text{ mHz}$  with ac voltage amplitude of  $\pm 10\text{ mV}$  using PAR M5210 lock-in amplifier connected to potentiostat/galvanostat.

After corrosion measurements, corroded surface samples was investigated with light microscope MXFMS-BD, Ningbo Sunny Instruments co.. Detailed surface morphology of the samples after the potentiodynamic measurements was examined by scanning electron microscope (SEM) Tescan Vega TS5136LS or JEOL JSM 5600. The quantitative analysis of the elements on the electrode surface was determined by energy dispersive spectroscopy (EDS).

## Results and discussion

The influence of heat treatment procedures for cast CuAlNi alloy to its corrosion behavior in NaCl solution was investigated with different electrochemical methods. The results of potentiodynamic polarization measurements for CuAlNi alloy in 0.9% NaCl solution (as cast and heat treated) are shown on Figure 2.

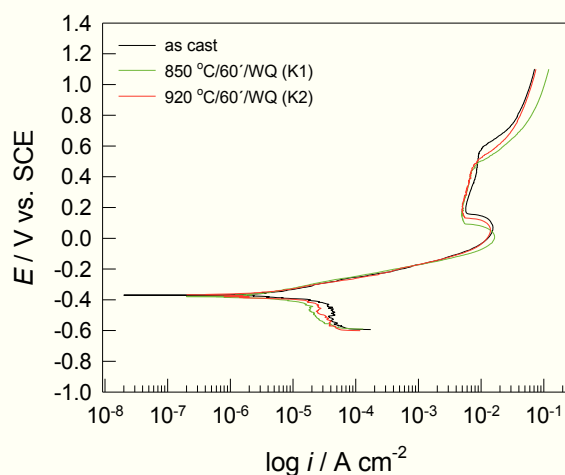


Figure 2. Potentiodynamic polarization curves for CuAlNi alloy as-cast and solution annealed state (K1 and K2) in 0.9% NaCl solution [38]

Presented potentiodynamic polarisation curves consist of cathodic branch which is the result of occurring cathodic reaction and the anode branch which is the result of occurring the anodic reaction, in this case alloy dissolution. Three different regions can be seen on anodic parts of polarization curves: the apparent Tafel region followed by a pseudo passive region and the third region in which current rises again. According to the literature, this anodic behaviour is characteristic for dissolution of copper and copper alloys [33,39,40]. Tafel region is characterised by dissolution of Cu and Al from the alloy surface and the formation of complexes ( $\text{CuCl}_2^-$ ) that diffuses from the surface of the electrode in a solution, while reduction in anodic current density in active-passive region, can be explained by the formation of low soluble surface corrosion products, probably cuprous chloride ( $\text{CuCl}$ ) and cuprous oxide ( $\text{Cu}_2\text{O}$ ), which have some protective effect and reduce the active dissolution of metals from the surface [16,41,42], or the formation of aluminium oxide/hydroxide layer, which has been found in the similar corrosion investigation on the surface of Cu–Al and Cu–Al–Ag alloys in  $0.5 \text{ mol dm}^{-3}$  NaCl solution [33]. Further potential increase leads to dissolution of corrosion products surface layer which is manifested by increasing the anodic current density and the alloy dissolution continues due to the formation of Cu(II) species [39]. The results of potentiodynamic polarisation measurements have shown almost identical values of corrosion potentials and slightly lower value of corrosion current for heat treated CuAlNi alloy which suggest beneficial influence of heat treatment on corrosion properties of alloy. Influence of temperature and pH of the electrolyte on values of polarization resistance and corrosion current density for as cast CuAlNi alloy in 0.9 % NaCl solution was presented on Figure 3 a) and b):

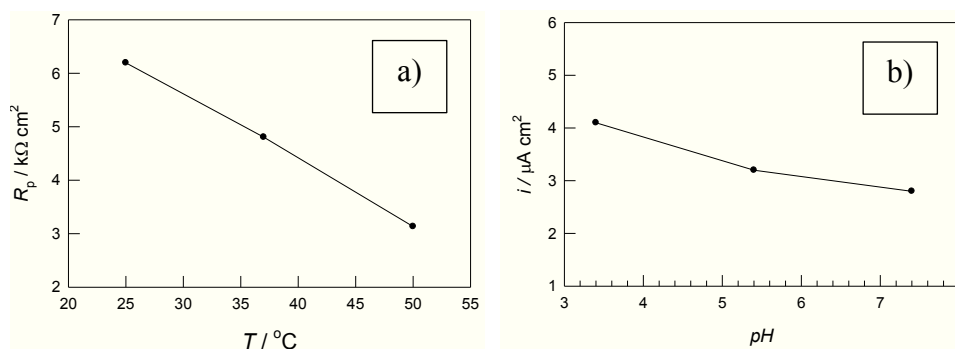


Figure 3. Influence of temperature a) and pH b) of 0.9 % NaCl solution on values of polarization resistance and corrosion current density for CuAlNi alloy



Increasing in electrolyte temperature and decreasing pH value have negative effect on corrosion stability of CuAlNi alloy what is manifested by lowering the values of polarization resistance and increasing the values of corrosion current density.

Results of analysis of corroded CuAlNi alloy surface is presented on Figure 4:

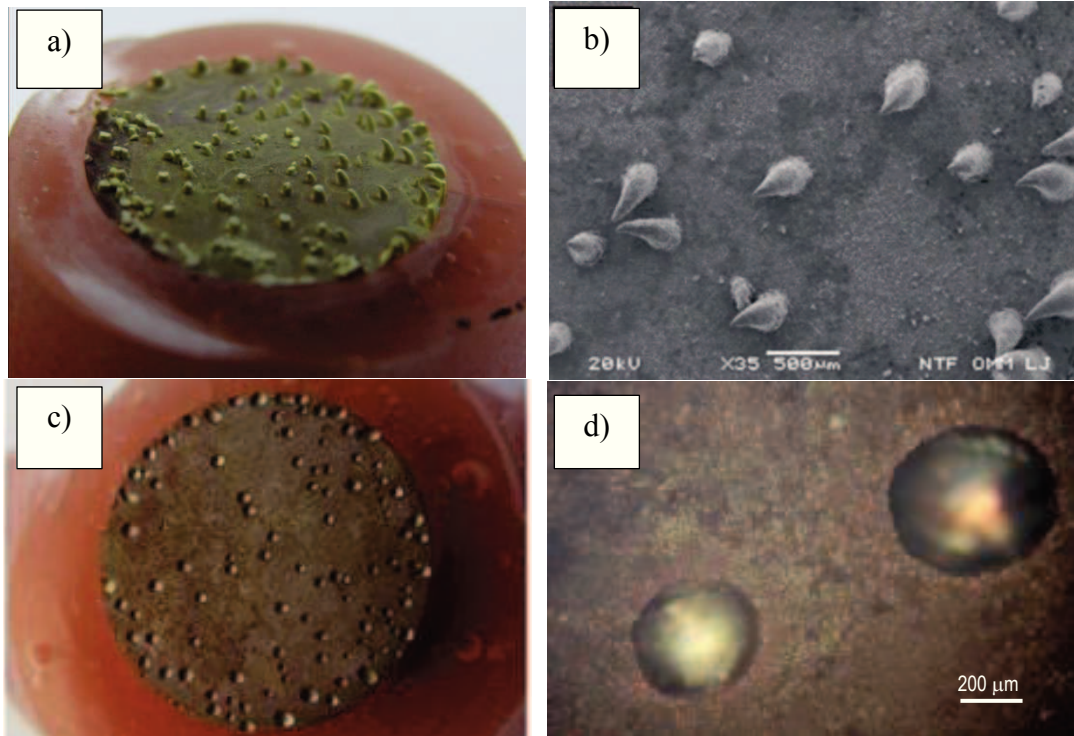


Figure 4. Surface analysis of CuAlNi alloy after polarization measurements in 0.9 % NaCl solution  
a) macro images of surface, b) SEM images of surface c) macro image of surface after ultrasonic treatment in deionised water, d) light microscopy image at 100 times magnification [43,44]

A large number of corrosion product deposits in the form of spikes can be observed on all CuAlNi electrodes surface and after their removal shallow pits have been discovered.

Intensive pitting corrosion also has been observed in corrosion investigation of CuAlNi alloy ribbons produced by melt spinning method in 0.9 % NaCl solution and can be seen on Figure 6.

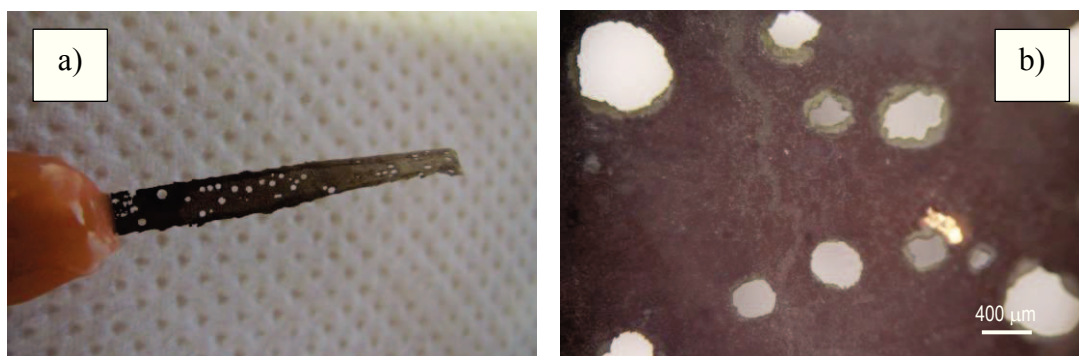


Figure 5. CuAlNi electrode after polarization measurements in 0.9% NaCl solution,  $T = 37^{\circ}\text{C}$ ,  $\text{pH} = 7.4$ : a) macro image and b) light microscope image with magnification of 50 times [45]

Detail information about alloy surface condition was achieved by SEM/EDS analysis (Figure 6).

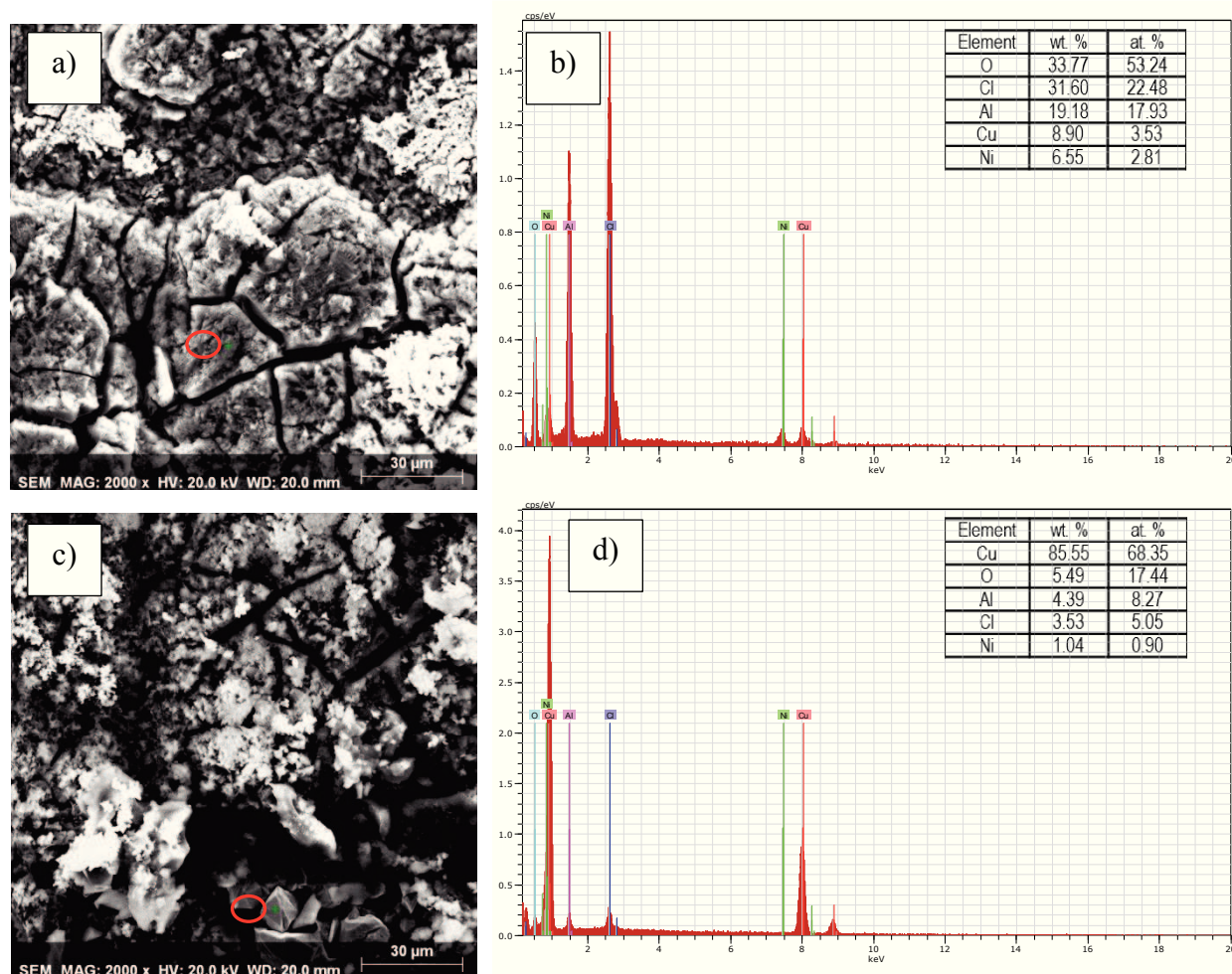


Figure 6. a) SEM images of the CuAlNi surface after potentiodynamic polarization measurement in 0.9% NaCl solution; b) related EDS analysis; c) SEM images of the Cu-Al-Ni surface after potentiodynamic polarization measurement in 1.5% NaCl solution; d) related EDS analysis [45]

EDS analysis have showed the presence of all alloying elements on the surfaces along with oxygen and chlorine, but in different percentage. According to the EDS data, after potentiodynamic polarization in 0.9 % NaCl solution, in some sites on the surface, dominant corrosion products on CuAlNi alloy surface are aluminium oxychloride compounds while after polarization in 1.5% NaCl solution dominant surface corrosion products are copper compounds with significant lower percentage of aluminium.

The influence of electrolyte pH and temperature on corrosion behaviour of as cast CuAlMn alloy (82.3 % Cu, 8.3 % Al and 9.4 % Mn) was investigated in 0.9% NaCl solution (pH =3.4, 5.4 and 7.4) at 37 °C and electrolyte temperatures of 25, 37 and 50 °C [46]. Increasing in electrolyte temperature as well as decreasing the electrolyte pH leads to the shifting the open circuit potential values in negative direction (Figure 7 a)), decreasing the polarization resistance value (Figure 7 b)) and increasing the corrosion current density.



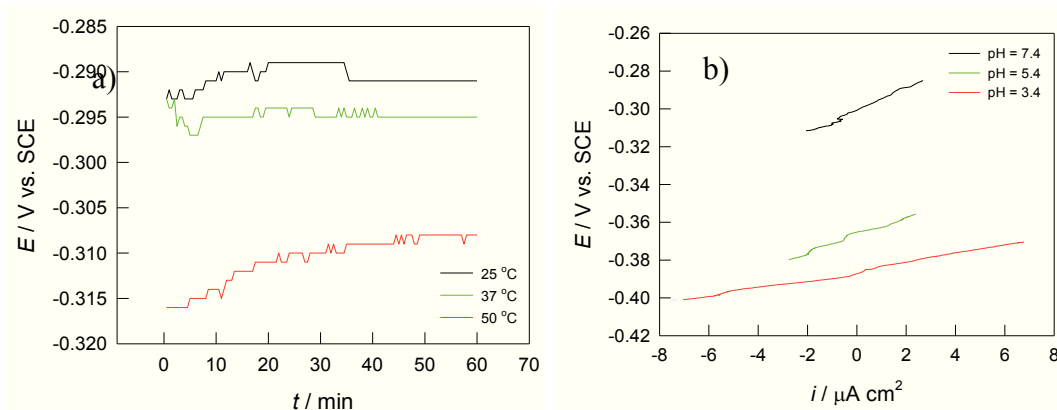


Figure 7. a) Open circuit potential measurement for CuAlMn alloy in 0.9% NaCl solution of different pH values; b) linear polarization curves for CuAlMn alloy, in 0.9% NaCl solution of different pH values

After potentiodynamic polarization measurement rough corroded surface of CuAlMn alloy was observed with light microscope examination (Figure 8).

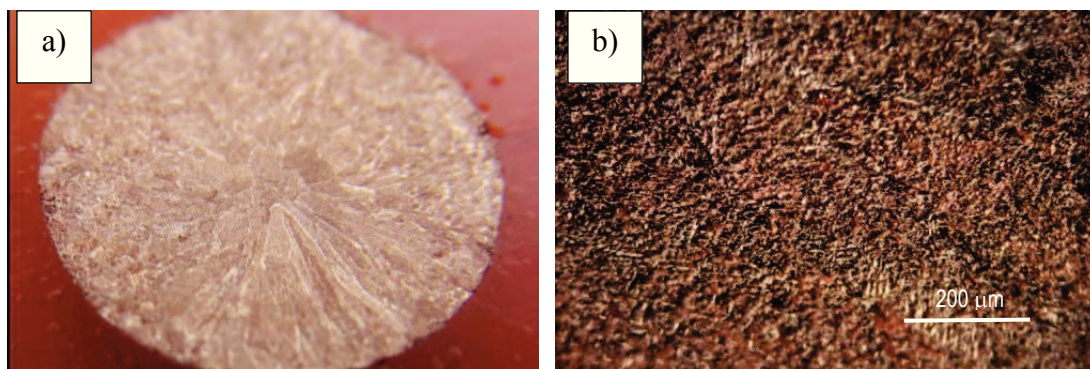


Figure 8. The CuAlMn electrode surface after polarization measurements in 0.9% NaCl solution,  $T = 37^{\circ}\text{C}$ ,  $\text{pH} = 3.4$ : a) photo camera macro image; b) light microscope image with 200 times magnification

It interesting to note that no pitting corrosion has been observed on the CuAlMn alloy surface after polarization measurements.

SEM/EDS analysis revealed some sites with corrosion product complex structure and composition, as can be seen on the Figure 9.

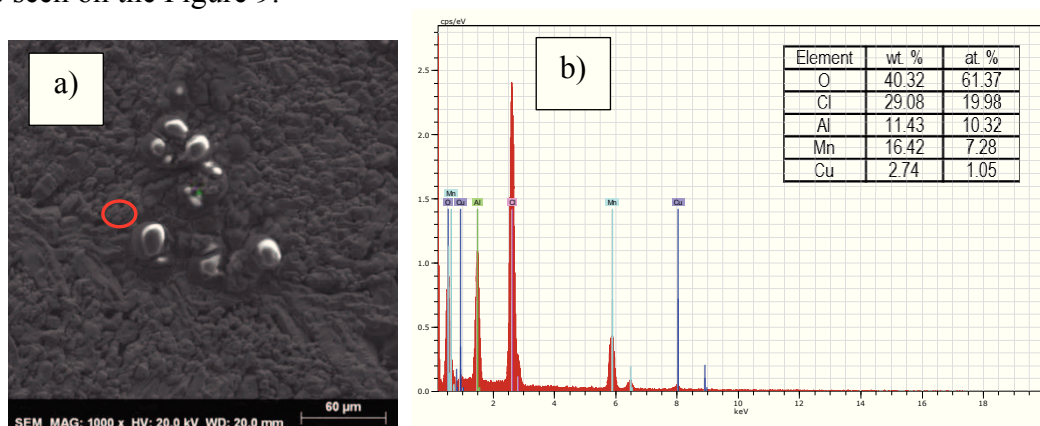


Figure 9. a) SEM images of the CuAlMn surface after potentiodynamic polarization measurement in 0.9% NaCl solution ( $T = 37^{\circ}\text{C}$ ,  $\text{pH} = 5.4$ ); b) related EDS analysis



The influence of Mn content on corrosion behaviour of CuAlMn alloy in 0.9% NaCl solution (pH = 7.4 and  $T = 37^{\circ}\text{C}$ ) was investigated using different electrochemical methods [47]. Investigations were performed on CuAlMn alloy ribbon samples with different composition: Cu-12%Al-4%Mn (sample A), Cu-12.3%Al-5.2%-Mn (sample B) and Cu-12%Al-6%Mn (sample C). The results of electrochemical impedance spectroscopy measurements were presented as Nyquist plots on Figure 10, along with the equivalent circuit which were used to fit experimental data. The response of the systems in the Nyquist complex plane was a semicircle whose diameter is growing with increasing manganese content.

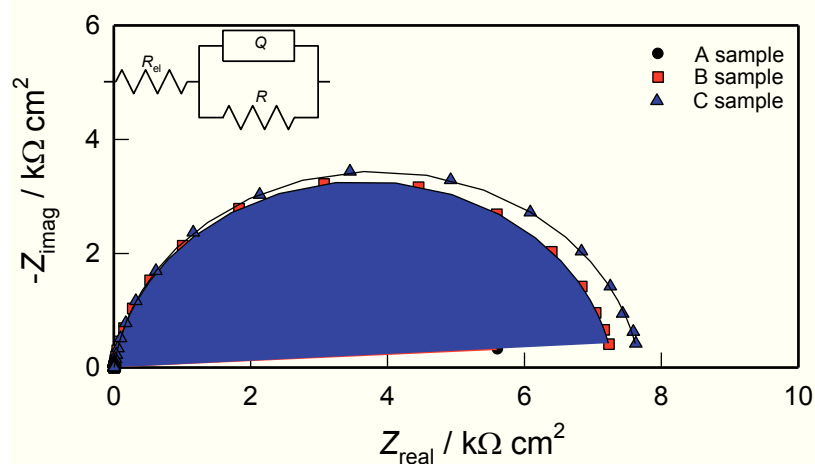


Figure 10. Nyquist plots for investigated CuAlMn alloys in 0.9% NaCl solution and proposed equivalent circuit [47]

The parameters of the equivalent circuit  $R_{el}$ ,  $R$  and  $Q$  were evaluated using a simple least square fit procedure and are presented in Table 2.

Table 1. Impedance parameters of investigated CuAlMn alloys in 0.9% NaCl solution

Alloy	$R_{el}$ ( $\Omega \text{ cm}^2$ )	$Q \times 10^6$ ( $\Omega^{-1} \text{ s}^n \text{ cm}^{-2}$ )	$n_1$	$R$ ( $\text{k}\Omega \text{ cm}^2$ )
A	8.31	44.75	0.91	5.24
B	8.04	38.62	0.93	6.53
C	7.78	34.21	0.93	7.18

From Table 1 can be seen that increase in Mn content lead to the increase in alloy surface film resistance ( $R$ ), while the surface layer capacity ( $Q$ ) decreases, which can be attributed to the increase of protective properties of the surface oxide layer on the electrode.

## Conclusions

Heat treatment procedure has beneficial effect on corrosion resistance of CuAlNi alloy in NaCl solution.

Decreasing pH value and increasing electrolyte temperature leads to more intensive corrosion attack on CuAlNi and CuAlMn alloy.

Dominant corrosion attack on CuAlNi alloy in chloride solution is pitting corrosion, while CuAlMn have higher resistance to pitting corrosion than CuAlNi alloy.

Increase in Mn content leads to increase in corrosion resistance of CuAlMn alloy.

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